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<p>(21) International Application Number: PCT/US00/11327</p> <p>(22) International Filing Date: 27 April 2000 (27.04.00)</p> <p>(30) Priority Data: 60/131,283 27 April 1999 (27.04.99) US 09/558,676 26 April 2000 (26.04.00) US </p> <p>(71) Applicant: SYMYX TECHNOLOGIES, INC. [US/US]; 3100 Central Expressway, Santa Clara, CA 95051 (US).</p> <p>(72) Inventor: GORER, Alexander; Symyx Technologies, Inc., 3100 Central Expressway, Santa Clara, CA 95051 (US).</p> <p>(74) Agents: HEJLEK, Edward, J. et al.; Senniger, Power, Leavitt and Roedel, 16th floor, One Metropolitan Square, St. Louis, MO 63102 (US).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>																									
<p>(54) Title: PLATINUM-RUTHENIUM-PALLADIUM-OSMIUM ALLOY FOR USE AS A FUEL CELL CATALYST</p> <p>(57) Abstract</p> <p>An improved noble metal alloy composition for a fuel cell catalyst, an alloy composition containing platinum, ruthenium, palladium and osmium. The alloy shows increased activity as compared to well-known catalysts.</p> <p style="text-align: center;"> Current Density as a Function of Voltage <i>Measured in Aqueous Methanol (0.1M) and H₂SO₄ (0.5M)</i> </p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Potential vs. NHE (V)</th> <th>Pt0.65Ru0.35 (A/cm²)</th> <th>Pd0.3Ru0.4Pt0.3 (A/cm²)</th> <th>Pt0.43Pd0.24Ru0.22Os0.11 (A/cm²)</th> </tr> </thead> <tbody> <tr> <td>0.20</td> <td>0.0005</td> <td>0.0004</td> <td>0.0004</td> </tr> <tr> <td>0.25</td> <td>0.0006</td> <td>0.0005</td> <td>0.0005</td> </tr> <tr> <td>0.30</td> <td>0.0010</td> <td>0.0008</td> <td>0.0008</td> </tr> <tr> <td>0.35</td> <td>0.0030</td> <td>0.0020</td> <td>0.0012</td> </tr> <tr> <td>0.40</td> <td>0.0090</td> <td>0.0060</td> <td>0.0030</td> </tr> </tbody> </table>				Potential vs. NHE (V)	Pt0.65Ru0.35 (A/cm²)	Pd0.3Ru0.4Pt0.3 (A/cm²)	Pt0.43Pd0.24Ru0.22Os0.11 (A/cm²)	0.20	0.0005	0.0004	0.0004	0.25	0.0006	0.0005	0.0005	0.30	0.0010	0.0008	0.0008	0.35	0.0030	0.0020	0.0012	0.40	0.0090	0.0060	0.0030
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PLATINUM-RUTHENIUM-PALLADIUM-OSMIUM ALLOYFOR USE AS A FUEL CELL CATALYSTBACKGROUND OF THE INVENTIONField of The Invention

5 The present invention relates to noble metal alloy catalysts, especially to platinum, palladium, ruthenium and osmium alloy catalysts, which are useful in fuel cell electrodes and other catalytic structures.

Background Information

10 A fuel cell is an electrochemical device for directly converting the chemical energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied thereto into a low-voltage direct current. 15 Thus, fuel cells chemically combine the molecules of a fuel and an oxidizer without burning, dispensing with the inefficiencies and pollution of traditional combustion.

20 A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer electrode (cathode), an electrolyte interposed between the electrodes (alkaline or acidic), and means for separately supplying a stream of fuel and a stream of oxidizer to the anode and the cathode, respectively. In operation, fuel supplied to the anode is oxidized releasing electrons which are conducted via an 25 external circuit to the cathode. At the cathode the supplied electrons are consumed when the oxidizer is reduced. The current flowing through the external circuit can be made to do useful work.

28 There are several types of fuel cells, including:
30 phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton exchange membrane. A phosphoric acid fuel cell operates at about 160-220°C, and preferably at about 190-200°C. This type of fuel cell is currently being used for multi-megawatt utility power generation and for co-
35 generation systems (i.e., combined heat and power generation) in the 50 to several hundred kilowatts range.

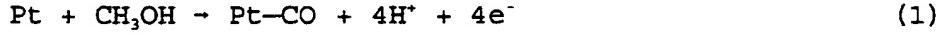
In contrast, proton exchange membrane fuel cells use a solid proton-conducting polymer membrane as the electrolyte. Typically, the polymer membrane must be maintained in a hydrated form during operation in order to prevent loss of ionic conduction which limits the operation temperature typically to about 70-120°C depending on the operating pressure, and preferably below about 100°C. Proton exchange membrane fuel cells have a much higher power density than liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small scale residential power generation where quick startup is required.

Conventional fuel cells use hydrogen gas as the fuel. Pure hydrogen gas, however, is difficult and costly to supply. Thus, hydrogen gas is typically supplied to a fuel cell using a reformer, which steam-reforms methanol and water at 200-300°C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformat gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). This process is also complex, adds cost and has the potential for producing undesirable pollutants. The conversion of a liquid fuel directly into electricity would be desirable, as then a high storage density, system simplicity and retention of existing fueling infrastructure could be combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost and is produced from renewable resources. Thus, a relatively new type of fuel cell has been the subject of a great amount of interest - the direct methanol fuel cell. In a direct methanol fuel cell, the overall process that occurs is that methanol and oxygen react to form water and carbon dioxide and electricity, i.e., methanol combustion.

For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst

materials are required at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au) because they are able 5 to withstand the corrosive environment - platinum being the most efficient and stable single-metal catalyst for fuel cells operating below about 300°C. While these elements were first used in solid form, later techniques were developed to disperse these metals over the surface of 10 electrically conductive supports (e.g., carbon black) to increase the surface area of the catalyst which in turn increased the number of reactive sites leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because the presence of 15 electrolyte, high temperatures and molecular oxygen dissolve the catalyst and/or sinter the dispersed catalyst by surface migration or dissolution/re-precipitation (see, e.g., U.S. Pat. No. 5,316,990).

Although platinum is a good catalyst, 20 concentrations of carbon monoxide (CO) above about 10 ppm in the fuel can rapidly poison the catalyst surface. As a result, platinum is a poor catalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels 25 (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H₂O plays a key role in the removal of such poisoning species in accordance with the following 30 reactions:



As indicated by the foregoing reactions, the methanol is 35 adsorbed and partially oxidized by platinum on the surface of the electrode (2). Adsorbed OH, from the hydrolysis of water (3), reacts with the adsorbed CO to produce carbon dioxide and a proton. However, platinum does not adsorb H₂O species well at the potentials fuel cell electrodes operate

(e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal thereby poisoning the catalyst. This applies in particular to a Proton exchange membrane fuel cell which is especially sensitive to CO poisoning as a result of its low operating temperatures.

One technique for alleviating fuel cell performance reduction due to anode CO poisoning is to employ an anode electrocatalyst which is itself more poison tolerant, but which still functions as a hydrogen oxidation catalyst in the presence of carbon monoxide. It is known that the tolerance of platinum poisoning by carbon monoxide is improved by alloying the platinum with ruthenium, preferably compositions centered around 50:50 atomic ratio (see, e.g., D. Chu and S. Gillman, *J. Electrochem. Soc.* 1996, 143, 1685).

It has been reported that the success of the platinum-ruthenium catalyst alloys is based on the ability of ruthenium to adsorb H₂O species at potentials where methanol is adsorbing on the platinum and facilitate the carbon monoxide removal reaction. This dual function, that is, to adsorb both reactants on the catalyst surface on adjacent metal sites, is known as the bifunctional mechanism in accordance with the following reaction:



It has been suggested that having platinum and ruthenium in adjacent sites forms an active site on the catalyst surface where methanol is oxidized in a less poisoning manner because the adjacent metal atoms are more efficiently adsorbing the methanol and the water reactants.

Although knowledge of phase equilibria and heuristic bond strength/activity relationships provide some guidance in the search for more effective catalyst compositions, there is at present no way to calculate the chemical composition of different metals that will afford the best catalyst activity for the direct methanol-air fuel cell reaction. As such, the search continues for stable, CO poisoning resistant and less costly catalysts having increased electrochemical activities.

BRIEF SUMMARY OF THE INVENTION

Among the objects of the invention are the preparation of catalysts based on platinum, ruthenium, palladium and osmium which have a high resistance to
5 poisoning by carbon monoxide thereby improving the efficiency of a fuel cell, decreasing the size of a fuel cell and reducing the cost of operating a fuel cell.

Briefly, therefore, the present invention is directed to a catalyst composition for use in
10 electrochemical reactor devices. The catalyst composition comprises platinum, ruthenium, palladium and osmium.

Also, the present invention is directed to a metal alloy composition comprising platinum, ruthenium, palladium and osmium.

15 Additionally, the present invention is directed to a fuel cell electrode comprising a catalyst dispersed on the surface of an electrically conductive support, the catalyst comprising platinum, ruthenium, palladium and osmium.

20 The present invention is further directed a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and an electrocatalyst for the catalytic oxidation of a hydrogen-containing fuel. The electrocatalyst comprises a metal alloy comprising platinum, ruthenium, palladium and osmium.
25

In yet another aspect, the present invention is directed to a method for the electrochemical conversion of a hydrocarbon-based fuel and oxygen to water, carbon dioxide and electricity in a fuel cell comprising an anode, a
30 cathode, a proton exchange membrane electrolyte therebetween, and an electrically conductive external circuit connecting the anode and cathode. The method comprising contacting the hydrocarbon-based fuel with a metal alloy catalyst to catalytically oxidize the fuel, the catalyst comprising platinum, ruthenium, palladium and osmium.
35

The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawing.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

5 Fig. 1 is a schematic structural view showing essential members of a methanol fuel cell.

Fig. 2 is a side view of a methanol fuel cell.

Fig. 3 is a graph comparing the catalytic activity, at a constant voltage and as a function of time, 10 of several alloy compositions including PtRuPdOs alloys (Electrodes #2-16), PtPd binary alloys (Electrodes #17 and #18), and a PtRuPd ternary alloy (Electrode #1). The alloy compositions on Electrodes #1, #17 and #18 are not PtRuPdOs alloys - as such they are not within the scope of the 15 claimed invention.

Fig. 4 is a graph comparing the catalytic activity of a PtRuPdOs alloy composition to a PtRuPd ternary alloy composition and a PtRu binary composition as a function of voltage.

20 DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a multi-component noble metal alloy for use in fuel cells. In particular, the present invention is directed to alloy compositions comprising platinum, ruthenium, palladium and 25 osmium. Surprisingly, platinum-ruthenium-palladium-osmium alloy compositions possess significantly improved catalytic activity over platinum-ruthenium binary alloys and even previously reported platinum-ruthenium-palladium ternary alloys.

30 In general, the concentration of osmium in the alloy is at least about 1 atomic percent, and preferably at least about 4 atomic percent. The concentration of osmium is typically less than about 30 atomic percent, and preferably less than about 25 atomic percent. Preferably, 35 the concentration of osmium is from about 4 atomic percent to about 16 atomic percent, and more preferably from about 5 atomic percent to about 14 atomic percent. The

concentration of platinum in the alloy is typically from about 20 atomic percent to about 60 atomic percent, preferably from about 25 atomic percent to about 55 atomic percent, more preferably from about 35 atomic percent to 5 about 55 atomic percent, and still more preferably from about 40 atomic percent to about 50 atomic percent. In general, the concentration of ruthenium in the alloy from about 10 atomic percent to about 40 atomic percent, preferably from about 15 atomic percent to about 35 atomic 10 percent, and more preferably from about 15 atomic percent to about 30 atomic percent. The concentration of palladium in the alloy is typically from about 5 atomic percent to about 35 atomic percent, preferably from about 10 atomic percent to about 30 atomic percent, more preferably from about 15 15 atomic percent to about 30 atomic percent, and still more preferably from about 20 atomic percent to about 30 atomic percent.

Experience to date suggests that when the combined concentrations of platinum and osmium are controlled within 20 a prescribed range, the alloy possesses significantly improved catalytic activity over certain platinum-ruthenium binary alloys and even certain previously reported platinum-ruthenium-palladium ternary alloys. As such, improved catalytic activity has been observed when the combined 25 concentrations of platinum and osmium are controlled such that the sum is from about from about 25 atomic percent to about 85 atomic percent, preferably from about 30 atomic percent to about 80 atomic percent, more preferably from about 35 atomic percent to about 75 atomic percent, still 30 more preferably from about 40 atomic percent to about 70 percent, and even more preferably between about 45 atomic percent and about 65 atomic percent. Alternatively, the foregoing improvement in catalytic activity has been observed by controlling the combined concentrations 35 ruthenium and palladium such that the sum is from about from about 15 atomic percent to about 75 atomic percent, preferably from about 20 atomic percent to about 70 atomic percent, more preferably from about 25 atomic percent to about 65 atomic percent, still more preferably from about 30

atomic percent to about 60 percent, and even more preferably between about 35 atomic percent and about 55 atomic percent.

In one embodiment of the present invention, therefore, the PtRuPdOs alloy contains, in atomic percentages, about 20% to about 60% platinum, about 10% to about 40% ruthenium, about 5% to about 35% palladium, and less than about 30% osmium. In another embodiment of the present invention the PtRuPdOs alloy contains, in atomic percentages, about 25% to about 55% platinum, about 15% to about 35% ruthenium, about 10% to about 30% palladium, and less than about 25% osmium. In another embodiment of the present invention, the PtRuPdOs alloy contains, in atomic percentages, about 35% to about 55% platinum, about 15% to about 35% ruthenium, about 15% to about 30% palladium, and about 4% to about 16% osmium. In a further embodiment of the present invention, the PtRuPdOs alloy contains, in atomic percentages, about 40% to about 50% platinum, about 15% to about 30% ruthenium, about 20% to about 30% palladium, and about 5 to about 14% osmium. Specific alloys which have been found to exhibit a relatively high methanol oxidation activity include the alloys corresponding the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x, y and z have the following values.

	x	y	z
25	43	22	24
	39	28	28
	51	15	20
	36	32	28
	54	14	18
30	52	15	15
	55	15	14
	54	16	10
	53	16	10

Although the PtRuPdOs alloy compositions of the present invention can be used in a phosphoric acid fuel cell, they are particularly useful in a direct methanol fuel cell. As shown in Fig. 1 and Fig. 2, a direct methanol fuel cell has a methanol electrode (fuel electrode or anode) 2 and an air electrode (oxidizer electrode or cathode) 3. In between the electrodes, a proton exchange membrane 3 serves as an electrolyte.

Preferably, in a fuel cell according to the present invention, the proton exchange membrane 1, the anode 2 and the cathode 3 are integrated into one body, and thus there is no contact resistance between the electrodes 2 and 3 and the proton exchange membrane 1. Current collectors 4 and 5 are at the anode and cathode, respectively. A methanol fuel chamber is indicated by numeral 8 and an air chamber is indicated by numeral 9. Numeral 6 is a sealant for the methanol fuel chamber and numeral 7 is a sealant for the air chamber. It is desirable to use a strongly acidic ion exchange membrane (e.g., perfluorosulphonic acid based membranes are widely used).

In general, electricity is generated by methanol combustion (i.e., methanol and oxygen react to form water, carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing the methanol into the methanol fuel chamber 8, while oxygen, preferably air is introduced into the air chamber 9, whereby an electric current can be immediately withdrawn therefrom into an outer circuit. Ideally, the methanol is oxidized at the anode to produce carbon dioxide gas, hydrogen ions and electrons. The thus formed hydrogen ions migrate through the strongly acidic proton exchange membrane 1 and react with oxygen and electrons from the outer circuit at the cathode 3 to form water. Typically, the methanol is introduced as a dilute acidic solution to enhance the chemical reaction thereby increasing power output (e.g., a 0.1 M methanol/0.5 M sulfuric acid solution).

Typically, the proton exchange membranes must remain hydrated during operation of the fuel cell in order to prevent loss of ionic conduction, thus the membrane is

preferably heat-resistant up to about 100-120°C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g., <10 Ω•cm), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic, this ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the membranes is typically between 50 and 200 μm. In general, the foregoing properties are achieved with materials which have no aliphatic hydrogen-carbon bonds, which, for example, is achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as Nafion® and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. Nafion® is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C-H bonds which, in a plasma polymer, do not form any aliphatic H atoms which could constitute attack sites for oxidative breakdown.

In general, the electrodes of the present invention comprise an electrically conductive material and are in contact with the PdRuPtOs catalyst of the present invention. The electrically conductive support is typically inorganic, preferably a carbon support. The carbon supports may be predominantly amorphous or graphitic. They may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. For example, it may be oil furnace black, acetylene black, graphite paper, carbon

fabric or carbon aerogel. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between the reactant (i.e., fuel or oxygen), the electrolyte and the electrocatalyst. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and products, particularly water to diffuse out of the electrode. Preferably, carbon black supports have a Brunauer, Emmett and Teller (BET) surface area of between 0 and 2000 m²/g, and preferably between 30 and 400 m²/g, more preferably between 60 to 250 m²/g. On the other hand, the carbon aerogel preferably has an electrical conductivity of between 10⁻² and 10³ Ω⁻¹•cm⁻¹ and a density of between 0.06 and 0.7 g/cm³; the pore size is between 20 and 100 nm (porosity up to about 95%).

Preferably, the proton exchange membrane, electrodes and catalyst materials are in contact. This is generally accomplished by depositing the catalyst either on the electrode, or the proton exchange membrane, and then the electrode and membrane placed in contact. The alloy catalysts of this invention can be deposited on either substrate by a variety of methods, including, plasma deposition, powder application, chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50 μm, preferably between 5 and 20 μm) of a catalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienylplatinum is gaseous between 10⁻⁴ and 10 mbar and can be excited using radio-frequency, microwaves or an electron cyclotron resonance transmitter to deposit platinum on the membrane.

According to another procedure, catalyst powder is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of catalyst particles exceeds about 2 mg/cm² the inclusion of a binder such as

polytetrafluoroethylene is common. Further, the catalyst may be plated with dispersed relatively small particles, e.g., about 20-200 Å, more preferably about 20-100 Å. This increases the catalyst surface area which in turn increases 5 the number of reaction sites leading to improved cell efficiency. In one such chemical plating process, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous suspension (slurry) of compounds of metallic 10 components constituting the alloy to permit adsorption or impregnation of the metallic compounds or their ions on or in the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid or formalin is slowly added 15 dropwise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

The surface concentration of catalyst on the membrane or electrode is based in part on the desired power 20 output and cost for a particular fuel cell. In general, power output increases with increasing concentration, however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration 25 of catalyst is selected to meet the application requirements. For example, a fuel cell designed to meet the requirements of a demanding application such as an outer space vehicle will usually have a surface concentration of catalyst sufficient to maximize the fuel cell power output. 30 Preferably, the desired power output is obtained with as little catalyst as possible. Typically, it is desirable that about 0.25 to about 6 mg/cm² of catalyst particles be in contact with the electrodes. If the surface concentration of catalyst particles is less than about 0.25 mg/cm², the 35 cell performance usually declines, whereas, above about 6 mg/cm² the cell performance is usually not improved.

To promote contact between the collector, electrode, catalyst and membrane, the layers are usually compressed at high temperature. The housings of the

individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly. Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

In general, the catalyst and electrodes of the present invention may be used to catalyze any fuel containing hydrogen (e.g., hydrogen and reformed-hydrogen fuels). The improved catalytic activity of the PtRuPdOs alloys, however, are particularly realized in the catalysis of hydrocarbon-based fuels. Applicable hydrocarbon-based fuels include saturated hydrocarbons such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons such as methanol and ethanol; and fossil fuels such as gasoline and kerosene; and mixtures thereof. The most preferred fuel, however, is methanol.

To achieve the full ion-conducting property of proton exchange membranes, suitable acids (gases or liquids) are typically added to the fuel. For example, SO₂, SO₃, sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as trifluoroacetic acid, and volatile phosphoric acid compounds may be used (see, e.g., "Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

25 Definitions

Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the catalyst, when fabricated into an electrode, at a given electric potential, or efficiency (Volts). Additionally, because of differences in the geometric area of electrodes, when comparing different catalysts, activity is often expressed in terms of current density (A/cm²).

Example 1

A tremendous amount of research has concentrated on exploring the activity of surface modified binary, and to a much lesser extent ternary and quaternary, alloys of platinum in an attempt to both increase the efficiency of and reduce the amount of precious metals in the anode part

of the fuel cell. Although electrodeposition was explored as a route to the synthesis of anode materials (see, e.g., F. Richarz et al. *Surface Science*, 1995, 335, 361), only a few compositions were actually prepared, and these 5 compositions were made using traditional single point electrodeposition techniques.

In contrast, the catalyst alloy compositions of this invention were prepared using the combinatorial techniques disclosed in U.S. Patent Application No.

10 09/119,187, filed July 20, 1998. Specifically, an array of independent electrodes (with areas of between about 1 and 2 mm²) were fabricated on inert substrates (e.g., glass, quartz, sapphire alumina, plastics, and thermally treated silicon). The individual electrodes were located
15 substantially in the center of the substrate, and were connected to contact pads around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from conducting materials (e.g., gold, silver, platinum, copper or other commonly used
20 electrode materials). In a preferred embodiment, the arrays were fabricated on standard 3" (about 7.5 cm) thermally oxidized single crystal silicon wafers, and the electrodes were gold with surface areas of about 1.26 mm².

A patterned insulating layer covered the wires and an
25 inner portion of the peripheral contact pads, but left the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer). Because of the insulating layer, it is possible to connect a lead (e.g., an
30 alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer may be, for example, glass,
35 silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, titanium dioxide, hardened photoresist, or other suitable material known to be insulating in nature.

Once a suitable inert substrate was provided, in this case thermally oxidized single crystal silicon was selected, photolithographic techniques were used to design and fabricate electrode patterns on it. By applying a 5 predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing one or more metals over the entire surface and removing predetermined regions of 10 these metals (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

The fabricated arrays consisted of a plurality of individually addressable electrodes that were insulated from 15 each other (by adequate spacing) and from the substrate (fabricated on an insulating substrate), and whose interconnects were insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material).

20 Materials were deposited on the above described electrode arrays to prepare a library of compositions by the electrodeposition of species from solution using standard electrochemical methods. More specifically, the depositions were carried out by immersing the electrode array in a 25 standard electrochemical deposition chamber containing the array, a platinum mesh counter electrode, and a reference electrode (e.g., Ag/AgCl). The chamber was filled with a plating solution containing known amounts of source material to be deposited. By selecting a given electrode and 30 applying a predetermined potential for a predetermined amount of time, a particular composition of materials (which may or may not correspond to the exact composition of the plating solution) was deposited on the electrode surface. Variations in the compositions deposited may be obtained 35 either by directly changing the solution composition for each deposition or by using different electrochemical deposition techniques, or both. Examples of how one may change the electrode composition by changing the deposition technique can include: changing the deposition potential,

changing the length of the deposition time, varying the counter anions, using different concentrations of each species, and even using different electrochemical deposition programs (e.g., potentiostatic oxidation/reduction, 5 galvanostatic oxidation/reduction, potential square-wave voltammetry, potential stair-step voltammetry, etc.). In any event, through repeated deposition steps, a variety of materials were deposited on the array.

After synthesizing the various alloy compositions 10 on the array, the different alloys were screened for methanol oxidation to determine relative catalytic activity against a standard alloy composition.

Example 2

15 Using the procedures described in Example 1 to synthesize catalyst compositions by electrodeposition, the following aqueous stock solutions were prepared in 0.5 M sulfuric acid (H_2SO_4): 0.03 M platinum chloride (H_2PtCl_6), 0.05 M ruthenium chloride ($RuCl_3$), 0.03 M palladium chloride 20 ($PdCl_3$), and 0.03 M osmium chloride ($OsCl_3$). The sulfuric acid merely served as an electrolyte thereby increasing the plating efficiency. A standard plating solution was created by combining 15 ml of the platinum chloride stock solution and 12 ml of the ruthenium chloride stock solution. The 25 electrodes on the array were then immersed in the standard plating solution. A potential of -0.93 V vs Ag/AgCl was applied for 2 minutes to the first electrode (Electrode #17 in Fig. 3). The thickness of the layer deposited on the electrode ranged from about 1500 and about 2000 Å. The 30 composition of the PtRu alloy plated under these conditions is represented by the formula $Pt_{0.65}Ru_{0.35}$.

To synthesize a PtRuPd alloy composition, an aliquot of the palladium chloride stock solution (e.g., 1 ml) was added to the standard PtRu plating solution and an 35 electrode was then plated at -0.93 V vs. Ag/AgCl for 2 minutes (e.g. Electrode #1 corresponding to $Pt_{0.30}Ru_{0.40}Pd_{0.30}$). Similarly, to synthesize a PtRuPdOs alloy composition, aliquots of palladium chloride and osmium chloride stock

solutions were added to the standard PtRu plating solution and an electrode was plated under the same conditions.

The amount of osmium in subsequently deposited alloys was increased by adding osmium chloride stock

5 solution to the plating solution. Thus, a library of alloy compositions can be created by varying the relative amounts of different stock solutions in the plating solution (e.g., Electrodes #2-#16 in Fig. 3 were plated under identical conditions except that the relative amounts of the stock
10 solutions were varied).

After synthesizing the various alloy compositions on the array, the different compositions were screened for methanol oxidation activity by placing the array into an electrochemical cell, which was filled with a room

15 temperature solution of 1M methanol in 0.5 M H₂SO₄. The cell also contained in Hg/HgSO₄ reference electrode and a platinum mesh counter electrode. Chronoamperometry measurements (i.e., holding a given electrode at a given potential and measuring the current that passes as a function of time)
20 were then performed on all of the electrodes by pulsing each individual electrode to a potential of 0.3 V vs NHE (Normal Hydrogen Electrode) and holding it there for about 6 minutes while monitoring and recording the current that flowed. Of particular interest were alloy compositions which showed
25 improved catalytic activity as compared to PtRu binary alloys in general, and preferably PtRu binary alloys with a relatively high activity (e.g., Pt_{0.65}Ru_{0.35} and Pt_{0.50}Ru_{0.50}). Of even greater interest were alloy compositions which showed improved catalytic activity as compared to PtRuPd ternary
30 alloys in general, and preferably the PtRuPd ternary alloys with a relatively high activity (e.g., Pt_{0.30}Ru_{0.40}Pd_{0.30}).

Also of interest is the current v. time slope for the electrodes, and in particular, Electrodes #4 and #5 compared to that of Electrode #1. Specifically, the slope
35 of the data for Electrode #4 (Pt_{0.43}Ru_{0.22}Pd_{0.24}Os_{0.11}) and Electrode #5 (Pt_{0.39}Ru_{0.28}Pd_{0.28}Os_{0.05}) is less steep than that for Electrode #1 (Pt_{0.30}Ru_{0.40}Pd_{0.30}) which indicates that those PtRuPdOs alloys, in addition to being more active than the

PtRuPd alloy, may be more resistant to carbon monoxide poisoning than the PtRuPd alloy.

Several electroplated alloys were analyzed using x-ray fluorescence (XRF) to determine their compositions.

- 5 It is commonly accepted that chemical compositions determined using x-ray fluorescence are within about 5% of the actual composition. A comparison of relative oxidation current (normalized to the most active catalyst, the alloy on Electrode #4) for several of the alloy compositions in
 10 the library is provided in Table 1.

TABLE 1

	Pt in alloy (atomic %)	Ru in alloy (atomic %)	Pd in alloy (atomic %)	Os in alloy (atomic %)	Relative Oxidation Current	Electrode #
15	43	22	24	11	1	4
	39	28	28	5	0.96	3
	51	15	20	14	0.96	5
	36	32	28	4	0.83	2
	30	40	30	0	0.81	1
20	54	14	18	14	0.61	6
	52	15	15	18	0.53	9
	55	15	14	16	0.52	7
	54	16	10	20	0.38	12
	53	15	10	22	0.35	14
25	65	35	0	0	0.23	17
	50	50	0	0	0.21	18

All quaternary alloys listed in the above table have a relative methanol oxidation activity above the $\text{Pt}_{0.65}\text{Ru}_{0.35}$ and $\text{Pt}_{0.5}\text{Ru}_{0.50}$ alloys (i.e., Electrodes #17 and
 30 #18). Further, the above PtRuPdOs alloys which have a relative methanol oxidation activity above the $\text{Pt}_{0.30}\text{Ru}_{0.40}\text{Pd}_{0.30}$ alloy include: platinum at about 43%, ruthenium at about 22%, palladium at about 24%, and osmium at about 11%, the most preferred embodiment; platinum at about 39%, ruthenium
 35 at about 28%, palladium at about 28%, and osmium at about 5%; platinum at about 51%, ruthenium at about 15%, palladium

at about 20%, and osmium at about 14%; platinum at about 36%, ruthenium at about 32%, palladium at about 28%, and osmium at about 4%.

Three of the foregoing electroplated alloys were subjected to powder synthesizing to gain information relevant to producing a fuel cell with dispersed catalyst compositions of the present invention. First, the plating solutions deposited on Electrodes #1, #4 and #5 were plated on a larger area electrode (about 1 cm²) and the plated alloy was mechanically removed and its x-ray fluorescence (XRF) spectrum was measured. Then the alloys were synthesized in powder form using a co-precipitation technique which entails slow dropwise additions of a 0.2 M NaBH₄ solution into a solution containing H₂PtCl₆, RuCl₃, PdCl₃, and OsCl₃. The slurry was maintained at about 80°C for about 3 hours, filtered, vigorously washed with distilled water, and dried for about 4 hours at about 110°C. X-ray fluorescence was applied to the synthesized powder and the resultant spectrum was compared with that of the desired electroplated alloy. When the XRF spectra are identical, the composition of the powder and electroplate alloys are identical. Typically, several iterations of alloy precipitation are necessary to produce a powder alloy composition which corresponds to the electroplated alloy. For the Electrode #1 alloy, a precipitation solution containing 10 ml of 0.03 M H₂PtCl₆, 4 ml of 0.05 M RuCl₃, and 9 ml of 0.03 M PdCl₃, yielded a powder alloy catalyst of identical composition. The alloy powder was then analyzed with more precise techniques to confirm its composition. Rutherford backscattering spectroscopy determined that the chemical composition of the precipitated powder alloys corresponding to Electrodes #1, #4 and #5 were Pt_{0.3}Ru_{0.4}Pd_{0.3}, Pt_{0.43}Ru_{0.22}Pd_{0.24}O_{0.11}, and Pt_{0.51}Ru_{0.15}Pd_{0.20}O_{0.14} respectively. It is commonly accepted that the chemical compositions determined using the Rutherford backscattering method are within about 2% of the actual composition.

The activity of the most preferred alloy, Pt_{0.43}Ru_{0.22}Pd_{0.24}O_{0.11}, was also compared to that of Pt₆₅Ru₃₅ and Pt_{0.30}Ru_{0.40}Pd_{0.30} as a function of increasing voltage (see, Fig.

4). Fig. 4 indicates that the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy oxidizes methanol at lower electrical potentials than the $\text{Pt}_{0.30}\text{Ru}_{0.40}\text{Pd}_{0.30}$ alloy or the $\text{Pt}_{65}\text{Ru}_{35}$ alloy. Also, the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy has a greater catalytic activity for 5 a given potential than the binary or ternary alloys. Further, the difference in catalytic activity between the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy and the binary alloy or the ternary alloy increases with increasing voltage.

It is to be understood that the above description 10 is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should also be 15 determined with reference to the claims and the full scope of equivalents to which such claims are entitled. The disclosures of all articles, patents and references, including patent applications and publications, are incorporated herein by reference for all purposes..

WHAT IS CLAIMED IS

1. A catalyst composition for use in electrochemical reactor devices comprising platinum, ruthenium, palladium and osmium.
2. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of osmium is from about 1% to about 25%.
3. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of osmium is from about 5% to about 14%.
4. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 25% to about 85%.
5. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 35% to about 75%.
6. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 45% to about 65%.
7. The catalyst composition of claim 1 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 30% to about 60%.
8. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 20% to about 60%, the concentration of ruthenium is from about 10% to about 40%, the concentration of palladium is from about 5% to about 35%, and the concentration of osmium is less than about 30%.
5
9. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 35% to about 55%, the concentration of ruthenium is from

about 15% to about 35%, the concentration of palladium is from about 15% to about 30%, and the concentration of osmium is from about 4% to about 16%.

5

10. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

5

11. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is about 43%, the concentration of ruthenium is about 22%, the concentration of palladium is from about 24, and the concentration of osmium is about 11%.

12. A metal alloy composition comprising platinum, ruthenium, palladium and osmium.

13. The metal alloy composition of claim 12 characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.25 to about 0.55, y is from about 0.15 to about 0.35, and z is from about 0.10 to about 0.30.

14. The metal alloy composition of claim 13 where the difference between 1 and the sum of x, y and z is at least about 0.04.

15. The metal alloy composition of claim 13 where the difference between 1 and the sum of y and z is from about 0.40 to about 0.70.

16. The metal alloy composition of claim 13 where the difference between 1 and the sum of y and z is from about 0.45 to about 0.65.

17. The metal alloy composition of claim 13 where the sum of y and z is from about 0.35 to about 0.55.

18. A metal alloy composition of claim 12 characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.40 to about 0.50, y is from about 0.15 to about 0.30, and z is from about 0.20 to about 0.30.

19. The metal alloy composition of claim 13 where x is about 0.43, y is about 0.22, and z is about 0.24.

20. A fuel cell electrode, the electrode comprising a catalyst dispersed on the surface of an electrically conductive support, the catalyst comprising platinum, ruthenium, palladium and osmium.

21. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of osmium is from about 4% to about 16%.

22. The fuel cell electrode of claim 20 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 40% to about 70%.

23. The fuel cell electrode of claim 20 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 30% to about 60%.

24. The fuel cell electrode of claim 20 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 35% to about 55%.

25. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about 20% to about 60%, the concentration of ruthenium is from about 10% to about 40%, the concentration of palladium is from about 5% to about 35%, and the concentration of osmium is less than about 30%.

5

26. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about

35% to about 55%, the concentration of ruthenium is from about 15% to about 35%, the concentration of palladium is from about 15% to about 30%, and the concentration of osmium is from about 4% to about 16%.

27. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

28. A fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and an electrocatalyst for the catalytic oxidation of a hydrogen-containing fuel, the fuel cell characterized in that the electrocatalyst comprises a metal alloy comprising platinum, ruthenium, palladium and osmium.

29. The fuel cell of claim 28 wherein the electrocatalyst is characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.20 to about 0.60, y is from about 0.10 to about 0.40, and z is from about 0.05 to about 0.35.

30. The fuel cell of claim 29 where the difference between 1 and the sum of y and z is from about 0.45 to about 0.65.

31. The fuel cell of claim 29 where the sum of y and z is from about 0.30 to about 0.60.

32. The fuel cell of claim 28 wherein the electrocatalyst is on the surface of the proton exchange membrane and in contact with the anode.

33. The fuel cell of claim 28 wherein the electrocatalyst is on the surface of the anode and in contact with the proton exchange membrane.

34. A method for the electrochemical conversion of a hydrocarbon-based fuel and oxygen to water, carbon dioxide and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane electrolyte therebetween, an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrocarbon-based fuel with a metal alloy catalyst to catalytically oxidize the fuel, the catalyst comprising platinum, ruthenium, palladium and osmium.

5 35. The method of claim 34 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 40% to about 70%.

36. The method of claim 34 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 35% to about 55%.

5 37. The method of claim 34 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

1 / 3

FIG. 1

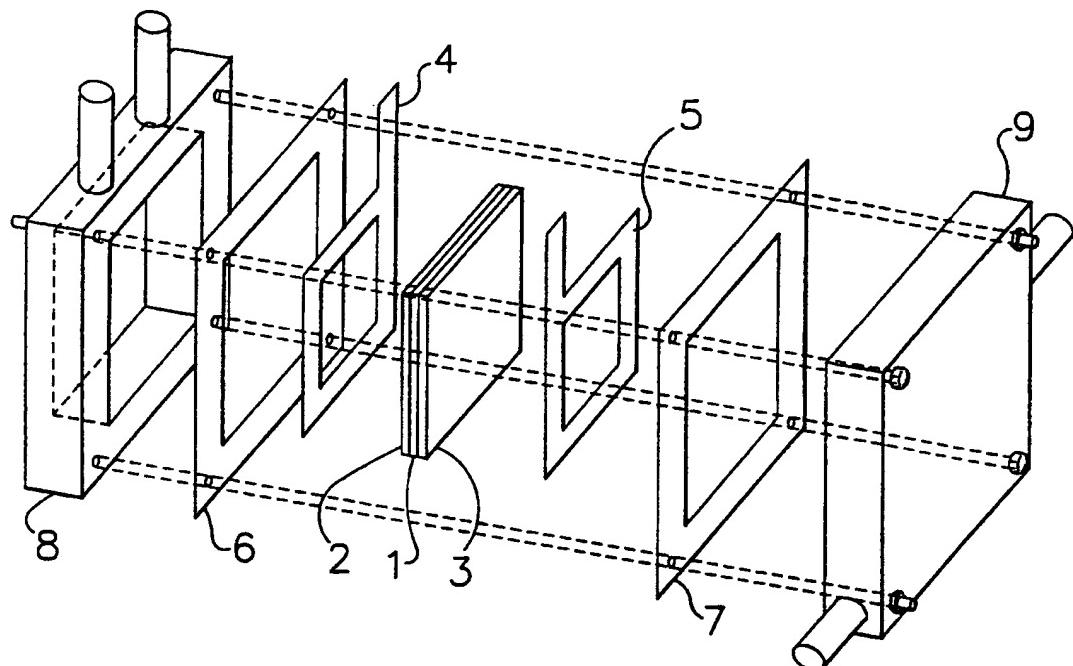
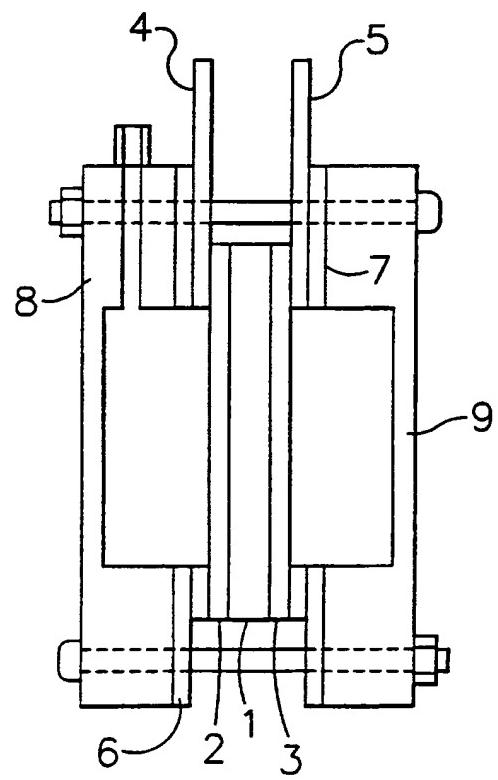
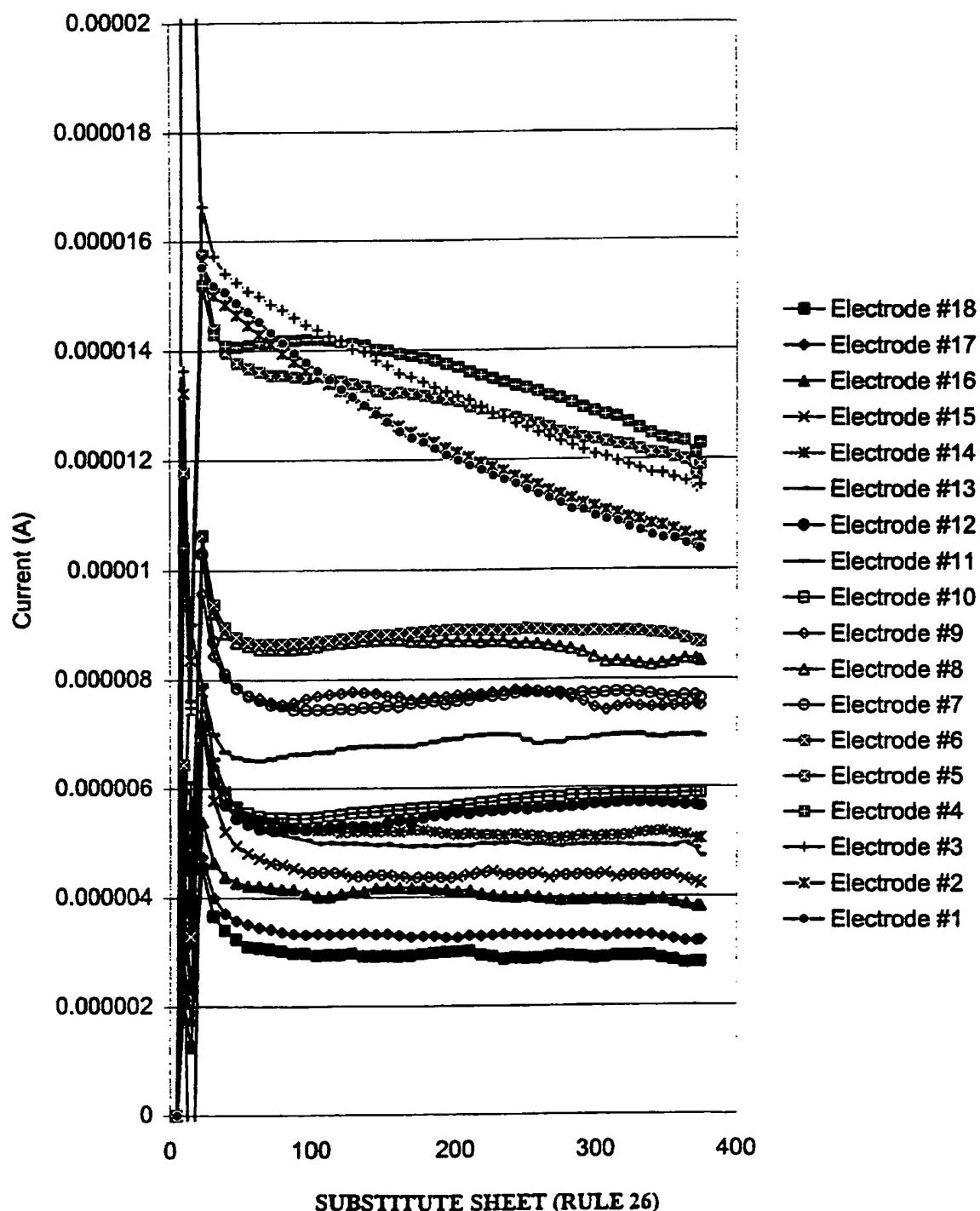


FIG. 2



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FIG. 3

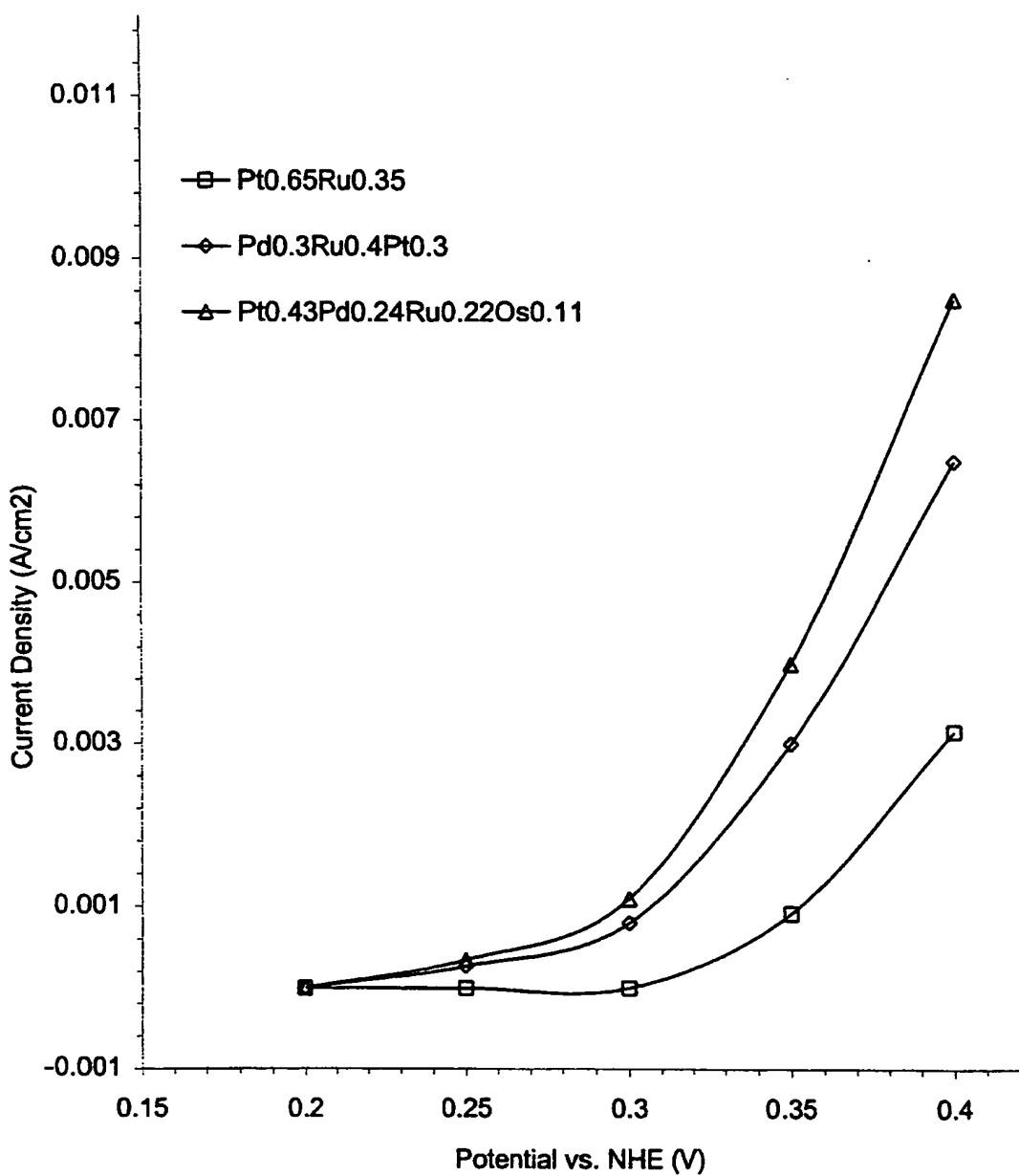
Methanol Oxidation Currents of Electroplated Alloy Compositions
-0.3 V vs. NHE

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3 / 3

FIG. 4

Current Density as a Function of Voltage
Measured in Aqueous Methanol (0.1M) and H₂SO₄ (0.5M)



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(74) Agents: HEJLEK, Edward, J. et al.; Senniger, Power, Leavitt and Roedel, 16th floor, One Metropolitan Square, St. Louis, MO 63102 (US).

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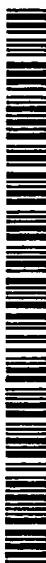
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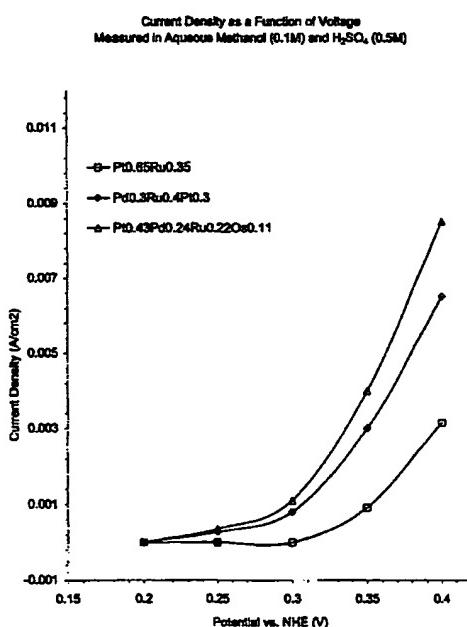
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(54) Title: PLATINUM-RUTHENIUM-PALLADIUM-OSMIUM ALLOY FOR USE AS A FUEL CELL CATALYST



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(57) Abstract: An improved noble metal alloy composition for a fuel cell catalyst, an alloy composition containing platinum, ruthenium, palladium and osmium. The alloy shows increased activity as compared to well-known catalysts.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M4/92 H01M8/10 B01J23/42 B01J23/46 B01J23/44
C22C5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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(74) Agents: **HEJLEK, Edward, J. et al.**; Senniger, Power, Leavitt and Roedel, 16th floor, One Metropolitan Square, St. Louis, MO 63102 (US).

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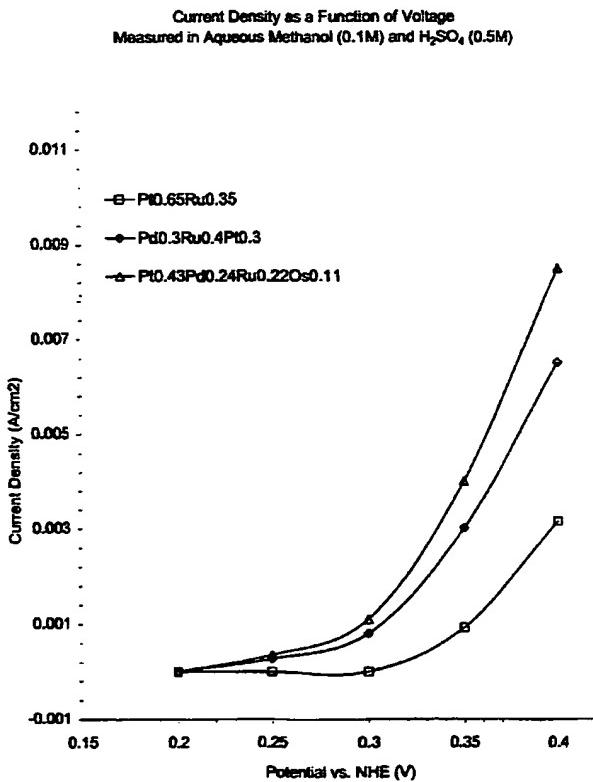
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[Continued on next page]

(54) Title: PLATINUM-RUTHENIUM-PALLADIUM-OSMIUM ALLOY FOR USE AS A FUEL CELL CATALYST



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(57) Abstract: An improved noble metal alloy composition for a fuel cell catalyst, an alloy composition containing platinum, ruthenium, palladium and osmium. The alloy shows increased activity as compared to well-known catalysts.



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PLATINUM-RUTHENIUM-PALLADIUM-OSMIUM ALLOYFOR USE AS A FUEL CELL CATALYSTBACKGROUND OF THE INVENTIONField of The Invention

5 The present invention relates to noble metal alloy catalysts, especially to platinum, palladium, ruthenium and osmium alloy catalysts, which are useful in fuel cell electrodes and other catalytic structures.

Background Information

10 A fuel cell is an electrochemical device for directly converting the chemical energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied thereto into a low-voltage direct current. 15 Thus, fuel cells chemically combine the molecules of a fuel and an oxidizer without burning, dispensing with the inefficiencies and pollution of traditional combustion.

20 A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer electrode (cathode), an electrolyte interposed between the electrodes (alkaline or acidic), and means for separately supplying a stream of fuel and a stream of oxidizer to the anode and the cathode, respectively. In operation, fuel supplied to the anode is oxidized releasing electrons which are conducted via an 25 external circuit to the cathode. At the cathode the supplied electrons are consumed when the oxidizer is reduced. The current flowing through the external circuit can be made to do useful work.

30 There are several types of fuel cells, including: phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton exchange membrane. A phosphoric acid fuel cell operates at about 160-220°C, and preferably at about 190-200°C. This type of fuel cell is currently being used for multi-megawatt utility power generation and for co-35 generation systems (i.e., combined heat and power generation) in the 50 to several hundred kilowatts range.

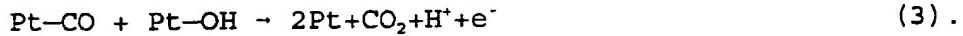
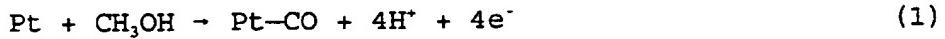
In contrast, proton exchange membrane fuel cells use a solid proton-conducting polymer membrane as the electrolyte. Typically, the polymer membrane must be maintained in a hydrated form during operation in order to prevent loss of ionic conduction which limits the operation temperature typically to about 70-120°C depending on the operating pressure, and preferably below about 100°C. Proton exchange membrane fuel cells have a much higher power density than liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small scale residential power generation where quick startup is required.

Conventional fuel cells use hydrogen gas as the fuel. Pure hydrogen gas, however, is difficult and costly to supply. Thus, hydrogen gas is typically supplied to a fuel cell using a reformer, which steam-reforms methanol and water at 200-300°C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformate gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). This process is also complex, adds cost and has the potential for producing undesirable pollutants. The conversion of a liquid fuel directly into electricity would be desirable, as then a high storage density, system simplicity and retention of existing fueling infrastructure could be combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost and is produced from renewable resources. Thus, a relatively new type of fuel cell has been the subject of a great amount of interest - the direct methanol fuel cell. In a direct methanol fuel cell, the overall process that occurs is that methanol and oxygen react to form water and carbon dioxide and electricity, i.e., methanol combustion.

For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst

materials are required at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au) because they are able 5 to withstand the corrosive environment - platinum being the most efficient and stable single-metal catalyst for fuel cells operating below about 300°C. While these elements were first used in solid form, later techniques were developed to disperse these metals over the surface of 10 electrically conductive supports (e.g., carbon black) to increase the surface area of the catalyst which in turn increased the number of reactive sites leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because the presence of 15 electrolyte, high temperatures and molecular oxygen dissolve the catalyst and/or sinter the dispersed catalyst by surface migration or dissolution/re-precipitation (see, e.g., U.S. Pat. No. 5,316,990).

Although platinum is a good catalyst, 20 concentrations of carbon monoxide (CO) above about 10 ppm in the fuel can rapidly poison the catalyst surface. As a result, platinum is a poor catalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels 25 (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H₂O plays a key role in the removal of such poisoning species in accordance with the following 30 reactions:

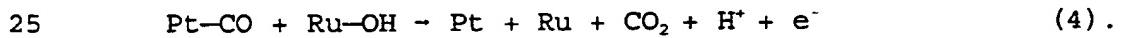


As indicated by the foregoing reactions, the methanol is 35 adsorbed and partially oxidized by platinum on the surface of the electrode (2). Adsorbed OH, from the hydrolysis of water (3), reacts with the adsorbed CO to produce carbon dioxide and a proton. However, platinum does not adsorb H₂O species well at the potentials fuel cell electrodes operate

(e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal thereby poisoning the catalyst. This applies in particular to a Proton exchange membrane fuel cell which is especially sensitive to CO poisoning as a result of its low operating temperatures.

One technique for alleviating fuel cell performance reduction due to anode CO poisoning is to employ an anode electrocatalyst which is itself more poison tolerant, but which still functions as a hydrogen oxidation catalyst in the presence of carbon monoxide. It is known that the tolerance of platinum poisoning by carbon monoxide is improved by alloying the platinum with ruthenium, preferably compositions centered around 50:50 atomic ratio (see, e.g., D. Chu and S. Gillman, *J. Electrochem. Soc.* 1996, 143, 1685).

It has been reported that the success of the platinum-ruthenium catalyst alloys is based on the ability of ruthenium to adsorb H₂O species at potentials where
20 methanol is adsorbing on the platinum and facilitate the carbon monoxide removal reaction. This dual function, that is, to adsorb both reactants on the catalyst surface on adjacent metal sites, is known as the bifunctional mechanism in accordance with the following reaction:



It has been suggested that having platinum and ruthenium in adjacent sites forms an active site on the catalyst surface where methanol is oxidized in a less poisoning manner because the adjacent metal atoms are more efficiently adsorbing the methanol and the water reactants.

Although knowledge of phase equilibria and heuristic bond strength/activity relationships provide some guidance in the search for more effective catalyst compositions, there is at present no way to calculate the chemical composition of different metals that will afford the best catalyst activity for the direct methanol-air fuel cell reaction. As such, the search continues for stable, CO poisoning resistant and less costly catalysts having increased electrochemical activities.

BRIEF SUMMARY OF THE INVENTION

Among the objects of the invention are the preparation of catalysts based on platinum, ruthenium, palladium and osmium which have a high resistance to 5 poisoning by carbon monoxide thereby improving the efficiency of a fuel cell, decreasing the size of a fuel cell and reducing the cost of operating a fuel cell.

Briefly, therefore, the present invention is directed to a catalyst composition for use in 10 electrochemical reactor devices. The catalyst composition comprises platinum, ruthenium, palladium and osmium.

Also, the present invention is directed to a metal alloy composition comprising platinum, ruthenium, palladium and osmium.

15 Additionally, the present invention is directed to a fuel cell electrode comprising a catalyst dispersed on the surface of an electrically conductive support, the catalyst comprising platinum, ruthenium, palladium and osmium.

20 The present invention is further directed a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and an electrocatalyst for the catalytic oxidation of a hydrogen-containing fuel. The electrocatalyst comprises a metal alloy comprising platinum, ruthenium, palladium and osmium.

25 In yet another aspect, the present invention is directed to a method for the electrochemical conversion of a hydrocarbon-based fuel and oxygen to water, carbon dioxide and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane electrolyte therebetween, and an electrically conductive external circuit connecting the anode and cathode. The method comprising contacting the hydrocarbon-based fuel with a metal alloy catalyst to catalytically oxidize the fuel, the 30 catalyst comprising platinum, ruthenium, palladium and osmium.

The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawing.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

5 Fig. 1 is a schematic structural view showing essential members of a methanol fuel cell.

Fig. 2 is a side view of a methanol fuel cell.

Fig. 3 is a graph comparing the catalytic activity, at a constant voltage and as a function of time, 10 of several alloy compositions including PtRuPdOs alloys (Electrodes #2-16), PtPd binary alloys (Electrodes #17 and #18), and a PtRuPd ternary alloy (Electrode #1). The alloy compositions on Electrodes #1, #17 and #18 are not PtRuPdOs alloys - as such they are not within the scope of the 15 claimed invention.

Fig. 4 is a graph comparing the catalytic activity of a PtRuPdOs alloy composition to a PtRuPd ternary alloy composition and a PtRu binary composition as a function of voltage.

20 DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a multi-component noble metal alloy for use in fuel cells. In particular, the present invention is directed to alloy compositions comprising platinum, ruthenium, palladium and 25 osmium. Surprisingly, platinum-ruthenium-palladium-osmium alloy compositions possess significantly improved catalytic activity over platinum-ruthenium binary alloys and even previously reported platinum-ruthenium-palladium ternary alloys.

30 In general, the concentration of osmium in the alloy is at least about 1 atomic percent, and preferably at least about 4 atomic percent. The concentration of osmium is typically less than about 30 atomic percent, and preferably less than about 25 atomic percent. Preferably, 35 the concentration of osmium is from about 4 atomic percent to about 16 atomic percent, and more preferably from about 5 atomic percent to about 14 atomic percent. The

concentration of platinum in the alloy is typically from about 20 atomic percent to about 60 atomic percent, preferably from about 25 atomic percent to about 55 atomic percent, more preferably from about 35 atomic percent to 5 about 55 atomic percent, and still more preferably from about 40 atomic percent to about 50 atomic percent. In general, the concentration of ruthenium in the alloy from about 10 atomic percent to about 40 atomic percent, preferably from about 15 atomic percent to about 35 atomic 10 percent, and more preferably from about 15 atomic percent to about 30 atomic percent. The concentration of palladium in the alloy is typically from about 5 atomic percent to about 35 atomic percent, preferably from about 10 atomic percent to about 30 atomic percent, more preferably from about 15 atomic 15 percent to about 30 atomic percent, and still more preferably from about 20 atomic percent to about 30 atomic percent.

Experience to date suggests that when the combined concentrations of platinum and osmium are controlled within 20 a prescribed range, the alloy possesses significantly improved catalytic activity over certain platinum-ruthenium binary alloys and even certain previously reported platinum-ruthenium-palladium ternary alloys. As such, improved catalytic activity has been observed when the combined 25 concentrations of platinum and osmium are controlled such that the sum is from about from about 25 atomic percent to about 85 atomic percent, preferably from about 30 atomic percent to about 80 atomic percent, more preferably from about 35 atomic percent to about 75 atomic percent, still 30 more preferably from about 40 atomic percent to about 70 percent, and even more preferably between about 45 atomic percent and about 65 atomic percent. Alternatively, the foregoing improvement in catalytic activity has been observed by controlling the combined concentrations 35 ruthenium and palladium such that the sum is from about from about 15 atomic percent to about 75 atomic percent, preferably from about 20 atomic percent to about 70 atomic percent, more preferably from about 25 atomic percent to about 65 atomic percent, still more preferably from about 30

atomic percent to about 60 percent, and even more preferably between about 35 atomic percent and about 55 atomic percent.

In one embodiment of the present invention, therefore, the PtRuPdOs alloy contains, in atomic percentages, about 20% to about 60% platinum, about 10% to about 40% ruthenium, about 5% to about 35% palladium, and less than about 30% osmium. In another embodiment of the present invention the PtRuPdOs alloy contains, in atomic percentages, about 25% to about 55% platinum, about 15% to about 35% ruthenium, about 10% to about 30% palladium, and less than about 25% osmium. In another embodiment of the present invention, the PtRuPdOs alloy contains, in atomic percentages, about 35% to about 55% platinum, about 15% to about 35% ruthenium, about 15% to about 30% palladium, and about 4% to about 16% osmium. In a further embodiment of the present invention, the PtRuPdOs alloy contains, in atomic percentages, about 40% to about 50% platinum, about 15% to about 30% ruthenium, about 20% to about 30% palladium, and about 5 to about 14% osmium. Specific alloys which have been found to exhibit a relatively high methanol oxidation activity include the alloys corresponding to the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x, y and z have the following values.

x	y	z
25	43	22
	39	28
	51	15
	36	32
	54	14
30	52	15
	55	15
	54	16
	53	16
		10

Although the PtRuPdOs alloy compositions of the present invention can be used in a phosphoric acid fuel cell, they are particularly useful in a direct methanol fuel cell. As shown in Fig. 1 and Fig. 2, a direct methanol fuel cell has a methanol electrode (fuel electrode or anode) 2 and an air electrode (oxidizer electrode or cathode) 3. In between the electrodes, a proton exchange membrane 1 serves as an electrolyte.

Preferably, in a fuel cell according to the present invention, the proton exchange membrane 1, the anode 2 and the cathode 3 are integrated into one body, and thus there is no contact resistance between the electrodes 2 and 3 and the proton exchange membrane 1. Current collectors 4 and 5 are at the anode and cathode, respectively. A methanol fuel chamber is indicated by numeral 8 and an air chamber is indicated by numeral 9. Numeral 6 is a sealant for the methanol fuel chamber and numeral 7 is a sealant for the air chamber. It is desirable to use a strongly acidic ion exchange membrane (e.g., perfluorosulphonic acid based membranes are widely used).

In general, electricity is generated by methanol combustion (i.e., methanol and oxygen react to form water, carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing the methanol into the methanol fuel chamber 8, while oxygen, preferably air is introduced into the air chamber 9, whereby an electric current can be immediately withdrawn therefrom into an outer circuit. Ideally, the methanol is oxidized at the anode to produce carbon dioxide gas, hydrogen ions and electrons. The thus formed hydrogen ions migrate through the strongly acidic proton exchange membrane 1 and react with oxygen and electrons from the outer circuit at the cathode 3 to form water. Typically, the methanol is introduced as a dilute acidic solution to enhance the chemical reaction thereby increasing power output (e.g., a 0.1 M methanol/0.5 M sulfuric acid solution).

Typically, the proton exchange membranes must remain hydrated during operation of the fuel cell in order to prevent loss of ionic conduction, thus the membrane is

preferably heat-resistant up to about 100-120°C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g., <10 Ω•cm), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic, this ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the membranes is typically between 50 and 200 μm. In general, the foregoing properties are achieved with materials which have no aliphatic hydrogen-carbon bonds, which, for example, is achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as Nafion® and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. Nafion® is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C-H bonds which, in a plasma polymer, do not form any aliphatic H atoms which could constitute attack sites for oxidative breakdown.

In general, the electrodes of the present invention comprise an electrically conductive material and are in contact with the PdRuPtOs catalyst of the present invention. The electrically conductive support is typically inorganic, preferably a carbon support. The carbon supports may be predominantly amorphous or graphitic. They may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. For example, it may be oil furnace black, acetylene black, graphite paper, carbon

fabric or carbon aerogel. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between the reactant (i.e., fuel or oxygen), the electrolyte and the electrocatalyst. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and products, particularly water to diffuse out of the electrode. Preferably, carbon black supports have a Brunauer, Emmett and Teller (BET) surface area of between 0 and 2000 m²/g, and preferably between 30 and 400 m²/g, more preferably between 60 to 250 m²/g. On the other hand, the carbon aerogel preferably has an electrical conductivity of between 10⁻² and 10³ Ω⁻¹•cm⁻¹ and a density of between 0.06 and 0.7 g/cm³; the pore size is between 20 and 100 nm (porosity up to about 95%).

Preferably, the proton exchange membrane, electrodes and catalyst materials are in contact.. This is generally accomplished by depositing the catalyst either on the electrode, or the proton exchange membrane, and then the electrode and membrane placed in contact. The alloy catalysts of this invention can be deposited on either substrate by a variety of methods, including, plasma deposition, powder application, chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50 μm, preferably between 5 and 20 μm) of a catalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienylplatinum is gaseous between 10⁻⁴ and 10 mbar and can be excited using radio-frequency, microwaves or an electron cyclotron resonance transmitter to deposit platinum on the membrane.

According to another procedure, catalyst powder is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of catalyst particles exceeds about 2 mg/cm² the inclusion of a binder such as

polytetrafluoroethylene is common. Further, the catalyst may be plated with dispersed relatively small particles, e.g., about 20-200 Å, more preferably about 20-100 Å. This increases the catalyst surface area which in turn increases 5 the number of reaction sites leading to improved cell efficiency. In one such chemical plating process, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous suspension (slurry) of compounds of metallic 10 components constituting the alloy to permit adsorption or impregnation of the metallic compounds or their ions on or in the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid or formalin is slowly added 15 dropwise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

The surface concentration of catalyst on the membrane or electrode is based in part on the desired power 20 output and cost for a particular fuel cell. In general, power output increases with increasing concentration, however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration 25 of catalyst is selected to meet the application requirements. For example, a fuel cell designed to meet the requirements of a demanding application such as an outer space vehicle will usually have a surface concentration of catalyst sufficient to maximize the fuel cell power output. 30 Preferably, the desired power output is obtained with as little catalyst as possible. Typically, it is desirable that about 0.25 to about 6 mg/cm² of catalyst particles be in contact with the electrodes. If the surface concentration of catalyst particles is less than about 0.25 mg/cm², the 35 cell performance usually declines, whereas, above about 6 mg/cm² the cell performance is usually not improved.

To promote contact between the collector, electrode, catalyst and membrane, the layers are usually compressed at high temperature. The housings of the

individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly. Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

In general, the catalyst and electrodes of the present invention may be used to catalyze any fuel containing hydrogen (e.g., hydrogen and reformed-hydrogen fuels). The improved catalytic activity of the PtRuPdOs alloys, however, are particularly realized in the catalysis of hydrocarbon-based fuels. Applicable hydrocarbon-based fuels include saturated hydrocarbons such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons such as methanol and ethanol; and fossil fuels such as gasoline and kerosene; and mixtures thereof. The most preferred fuel, however, is methanol.

To achieve the full ion-conducting property of proton exchange membranes, suitable acids (gases or liquids) are typically added to the fuel. For example, SO₂, SO₃, sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as trifluoroacetic acid, and volatile phosphoric acid compounds may be used (see, e.g., "Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

25 Definitions

Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the catalyst, when fabricated into an electrode, at a given electric potential, or efficiency (Volts). Additionally, because of differences in the geometric area of electrodes, when comparing different catalysts, activity is often expressed in terms of current density (A/cm²).

Example 1

A tremendous amount of research has concentrated on exploring the activity of surface modified binary, and to a much lesser extent ternary and quaternary, alloys of platinum in an attempt to both increase the efficiency of and reduce the amount of precious metals in the anode part

of the fuel cell. Although electrodeposition was explored as a route to the synthesis of anode materials (see, e.g., F. Richarz et al. *Surface Science*, 1995, 335, 361), only a few compositions were actually prepared, and these 5 compositions were made using traditional single point electrodeposition techniques.

In contrast, the catalyst alloy compositions of this invention were prepared using the combinatorial techniques disclosed in U.S. Patent Application No.

10 09/119,187, filed July 20, 1998. Specifically, an array of independent electrodes (with areas of between about 1 and 2 mm²) were fabricated on inert substrates (e.g., glass, quartz, sapphire alumina, plastics, and thermally treated silicon). The individual electrodes were located 15 substantially in the center of the substrate, and were connected to contact pads around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from conducting materials (e.g., gold, silver, platinum, copper or other commonly used 20 electrode materials). In a preferred embodiment, the arrays were fabricated on standard 3" (about 7.5 cm) thermally oxidized single crystal silicon wafers, and the electrodes were gold with surface areas of about 1.26 mm².

A patterned insulating layer covered the wires and an 25 inner portion of the peripheral contact pads, but left the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer). Because of the insulating layer, it is possible to connect a lead (e.g., an 30 alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer may be, for example, glass, 35 silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, titanium dioxide, hardened photoresist, or other suitable material known to be insulating in nature.

Once a suitable inert substrate was provided, in this case thermally oxidized single crystal silicon was selected, photolithographic techniques were used to design and fabricate electrode patterns on it. By applying a 5 predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing one or more metals over the entire surface and removing predetermined regions of 10 these metals (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

The fabricated arrays consisted of a plurality of individually addressable electrodes that were insulated from 15 each other (by adequate spacing) and from the substrate (fabricated on an insulating substrate), and whose interconnects were insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material).

20 Materials were deposited on the above described electrode arrays to prepare a library of compositions by the electrodeposition of species from solution using standard electrochemical methods. More specifically, the depositions were carried out by immersing the electrode array in a 25 standard electrochemical deposition chamber containing the array, a platinum mesh counter electrode, and a reference electrode (e.g., Ag/AgCl). The chamber was filled with a plating solution containing known amounts of source material to be deposited. By selecting a given electrode and 30 applying a predetermined potential for a predetermined amount of time, a particular composition of materials (which may or may not correspond to the exact composition of the plating solution) was deposited on the electrode surface. Variations in the compositions deposited may be obtained 35 either by directly changing the solution composition for each deposition or by using different electrochemical deposition techniques, or both. Examples of how one may change the electrode composition by changing the deposition technique can include: changing the deposition potential,

changing the length of the deposition time, varying the counter anions, using different concentrations of each species, and even using different electrochemical deposition programs (e.g., potentiostatic oxidation/reduction, 5 galvanostatic oxidation/reduction, potential square-wave voltammetry, potential stair-step voltammetry, etc.). In any event, through repeated deposition steps, a variety of materials were deposited on the array.

After synthesizing the various alloy compositions 10 on the array, the different alloys were screened for methanol oxidation to determine relative catalytic activity against a standard alloy composition.

Example 2

15 Using the procedures described in Example 1 to synthesize catalyst compositions by electrodeposition, the following aqueous stock solutions were prepared in 0.5 M sulfuric acid (H_2SO_4): 0.03 M platinum chloride (H_2PtCl_6), 0.05 M ruthenium chloride ($RuCl_3$), 0.03 M palladium chloride 20 ($PdCl_3$), and 0.03 M osmium chloride ($OsCl_3$). The sulfuric acid merely served as an electrolyte thereby increasing the plating efficiency. A standard plating solution was created by combining 15 ml of the platinum chloride stock solution and 12 ml of the ruthenium chloride stock solution. The 25 electrodes on the array were then immersed in the standard plating solution. A potential of -0.93 V vs Ag/AgCl was applied for 2 minutes to the first electrode (Electrode #17 in Fig. 3). The thickness of the layer deposited on the electrode ranged from about 1500 and about 2000 Å. The 30 composition of the PtRu alloy plated under these conditions is represented by the formula $Pt_{0.65}Ru_{0.35}$.

To synthesize a PtRuPd alloy composition, an aliquot of the palladium chloride stock solution (e.g., 1 ml) was added to the standard PtRu plating solution and an 35 electrode was then plated at -0.93 V vs. Ag/AgCl for 2 minutes (e.g. Electrode #1 corresponding to $Pt_{0.30}Ru_{0.40}Pd_{0.30}$). Similarly, to synthesize a PtRuPdOs alloy composition, aliquots of palladium chloride and osmium chloride stock

solutions were added to the standard PtRu plating solution and an electrode was plated under the same conditions.

The amount of osmium in subsequently deposited alloys was increased by adding osmium chloride stock 5 solution to the plating solution. Thus, a library of alloy compositions can be created by varying the relative amounts of different stock solutions in the plating solution (e.g., Electrodes #2-#16 in Fig. 3 were plated under identical conditions except that the relative amounts of the stock 10 solutions were varied).

After synthesizing the various alloy compositions on the array, the different compositions were screened for methanol oxidation activity by placing the array into an electrochemical cell, which was filled with a room 15 temperature solution of 1M methanol in 0.5 M H₂SO₄. The cell also contained in Hg/HgSO₄ reference electrode and a platinum mesh counter electrode. Chronoamperometry measurements (i.e., holding a given electrode at a given potential and measuring the current that passes as a function of time) 20 were then performed on all of the electrodes by pulsing each individual electrode to a potential of 0.3 V vs NHE (Normal Hydrogen Electrode) and holding it there for about 6 minutes while monitoring and recording the current that flowed. Of particular interest were alloy compositions which showed 25 improved catalytic activity as compared to PtRu binary alloys in general, and preferably PtRu binary alloys with a relatively high activity (e.g., Pt_{0.65}Ru_{0.35} and Pt_{0.50}Ru_{0.50}). Of even greater interest were alloy compositions which showed improved catalytic activity as compared to PtRuPd ternary 30 alloys in general, and preferably the PtRuPd ternary alloys with a relatively high activity (e.g., Pt_{0.30}Ru_{0.40}Pd_{0.30}).

Also of interest is the current v. time slope for the electrodes, and in particular, Electrodes #4 and #5 compared to that of Electrode #1. Specifically, the slope 35 of the data for Electrode #4 (Pt_{0.43}Ru_{0.22}Pd_{0.24}Os_{0.11}) and Electrode #5 (Pt_{0.39}Ru_{0.28}Pd_{0.28}Os_{0.05}) is less steep than that for Electrode #1 (Pt_{0.30}Ru_{0.40}Pd_{0.30}) which indicates that those PtRuPdOs alloys, in addition to being more active than the

PtRuPd alloy, may be more resistant to carbon monoxide poisoning than the PtRuPd alloy.

Several electroplated alloys were analyzed using x-ray fluorescence (XRF) to determine their compositions.

- 5 It is commonly accepted that chemical compositions determined using x-ray fluorescence are within about 5% of the actual composition. A comparison of relative oxidation current (normalized to the most active catalyst, the alloy on Electrode #4) for several of the alloy compositions in
 10 the library is provided in Table 1.

TABLE 1

	Pt in alloy (atomic %)	Ru in alloy (atomic %)	Pd in alloy (atomic %)	Os in alloy (atomic %)	Relative Oxidation Current	Electrode #
15	43	22	24	11	1	4
	39	28	28	5	0.96	3
	51	15	20	14	0.96	5
	36	32	28	4	0.83	2
	30	40	30	0	0.81	1
20	54	14	18	14	0.61	6
	52	15	15	18	0.53	9
	55	15	14	16	0.52	7
	54	16	10	20	0.38	12
	53	15	10	22	0.35	14
25	65	35	0	0	0.23	17
	50	50	0	0	0.21	18

All quaternary alloys listed in the above table have a relative methanol oxidation activity above the $\text{Pt}_{0.65}\text{Ru}_{0.35}$ and $\text{Pt}_{0.5}\text{Ru}_{0.50}$ alloys (i.e., Electrodes #17 and #18). Further, the above PtRuPdOs alloys which have a relative methanol oxidation activity above the $\text{Pt}_{0.30}\text{Ru}_{0.40}\text{Pd}_{0.30}$ alloy include: platinum at about 43%, ruthenium at about 22%, palladium at about 24%, and osmium at about 11%, the most preferred embodiment; platinum at about 39%, ruthenium at about 28%, palladium at about 28%, and osmium at about 5%; platinum at about 51%, ruthenium at about 15%, palladium

at about 20%, and osmium at about 14%; platinum at about 36%, ruthenium at about 32%, palladium at about 28%, and osmium at about 4%.

Three of the foregoing electroplated alloys were subjected to powder synthesizing to gain information relevant to producing a fuel cell with dispersed catalyst compositions of the present invention. First, the plating solutions deposited on Electrodes #1, #4 and #5 were plated on a larger area electrode (about 1 cm²) and the plated alloy was mechanically removed and its x-ray fluorescence (XRF) spectrum was measured. Then the alloys were synthesized in powder form using a co-precipitation technique which entails slow dropwise additions of a 0.2 M NaBH₄ solution into a solution containing H₂PtCl₆, RuCl₃, PdCl₃, and OsCl₃. The slurry was maintained at about 80°C for about 3 hours, filtered, vigorously washed with distilled water, and dried for about 4 hours at about 110°C. X-ray fluorescence was applied to the synthesized powder and the resultant spectrum was compared with that of the desired electroplated alloy. When the XRF spectra are identical, the composition of the powder and electroplate alloys are identical. Typically, several iterations of alloy precipitation are necessary to produce a powder alloy composition which corresponds to the electroplated alloy. For the Electrode #1 alloy, a precipitation solution containing 10 ml of 0.03 M H₂PtCl₆, 4 ml of 0.05 M RuCl₃, and 9 ml of 0.03 M PdCl₃, yielded a powder alloy catalyst of identical composition. The alloy powder was then analyzed with more precise techniques to confirm its composition. Rutherford backscattering spectroscopy determined that the chemical composition of the precipitated powder alloys corresponding to Electrodes #1, #4 and #5 were Pt_{0.3}Ru_{0.4}Pd_{0.3}, Pt_{0.43}Ru_{0.22}Pd_{0.24}Os_{0.11}, and Pt_{0.51}Ru_{0.15}Pd_{0.20}Os_{0.14} respectively. It is commonly accepted that the chemical compositions determined using the Rutherford backscattering method are within about 2% of the actual composition.

The activity of the most preferred alloy, Pt_{0.43}Ru_{0.22}Pd_{0.24}Os_{0.11}, was also compared to that of Pt₆₅Ru₃₅ and Pt_{0.30}Ru_{0.40}Pd_{0.30} as a function of increasing voltage (see, Fig.

4). Fig. 4 indicates that the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy oxidizes methanol at lower electrical potentials than the $\text{Pt}_{0.30}\text{Ru}_{0.40}\text{Pd}_{0.30}$ alloy or the $\text{Pt}_{65}\text{Ru}_{35}$ alloy. Also, the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy has a greater catalytic activity for 5 a given potential than the binary or ternary alloys. Further, the difference in catalytic activity between the $\text{Pt}_{0.43}\text{Ru}_{0.22}\text{Pd}_{0.24}\text{Os}_{0.11}$ alloy and the binary alloy or the ternary alloy increases with increasing voltage.

It is to be understood that the above description 10 is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should also be 15 determined with reference to the claims and the full scope of equivalents to which such claims are entitled. The disclosures of all articles, patents and references, including patent applications and publications, are incorporated herein by reference for all purposes.

WHAT IS CLAIMED IS

1. A catalyst composition for use in electrochemical reactor devices comprising platinum, ruthenium, palladium and osmium.

2. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of osmium is from about 1% to about 25%.

3. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of osmium is from about 5% to about 14%.

4. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 25% to about 85%.

5. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 35% to about 75%.

6. The catalyst composition of claim 1 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 45% to about 65%.

7. The catalyst composition of claim 1 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 30% to about 60%.

8. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 20% to about 60%, the concentration of ruthenium is from about 10% to about 40%, the concentration of palladium is from about 5% to about 35%, and the concentration of osmium is less than about 30%.

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9. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 35% to about 55%, the concentration of ruthenium is from

about 15% to about 35%, the concentration of palladium is from about 15% to about 30%, and the concentration of osmium is from about 4% to about 16%.

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10. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

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11. The catalyst composition of claim 1 wherein the concentration, in atomic percent, of platinum is about 43%, the concentration of ruthenium is about 22%, the concentration of palladium is from about 24, and the concentration of osmium is about 11%.

12. A metal alloy composition comprising platinum, ruthenium, palladium and osmium.

13. The metal alloy composition of claim 12 characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.25 to about 0.55, y is from about 0.15 to about 0.35, and z is from about 0.10 to about 0.30.

14. The metal alloy composition of claim 13 where the difference between 1 and the sum of x, y and z is at least about 0.04.

15. The metal alloy composition of claim 13 where the difference between 1 and the sum of y and z is from about 0.40 to about 0.70.

16. The metal alloy composition of claim 13 where the difference between 1 and the sum of y and z is from about 0.45 to about 0.65.

17. The metal alloy composition of claim 13 where the sum of y and z is from about 0.35 to about 0.55.

18. A metal alloy composition of claim 12 characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.40 to about 0.50, y is from about 0.15 to about 0.30, and z is from about 0.20 to about 0.30.

19. The metal alloy composition of claim 13 where x is about 0.43, y is about 0.22, and z is about 0.24.

20. A fuel cell electrode, the electrode comprising a catalyst dispersed on the surface of an electrically conductive support, the catalyst comprising platinum, ruthenium, palladium and osmium.

21. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of osmium is from about 4% to about 16%.

22. The fuel cell electrode of claim 20 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 40% to about 70%.

23. The fuel cell electrode of claim 20 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 30% to about 60%.

24. The fuel cell electrode of claim 20 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 35% to about 55%.

25. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about 20% to about 60%, the concentration of ruthenium is from about 10% to about 40%, the concentration of palladium is from about 5% to about 35%, and the concentration of osmium is less than about 30%.

26. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about

35% to about 55%, the concentration of ruthenium is from about 15% to about 35%, the concentration of palladium is from about 15% to about 30%, and the concentration of osmium is from about 4% to about 16%.

27. The fuel cell electrode of claim 20 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

28. A fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and an electrocatalyst for the catalytic oxidation of a hydrogen-containing fuel, the fuel cell characterized in that the electrocatalyst comprises a metal alloy comprising platinum, ruthenium, palladium and osmium.

29. The fuel cell of claim 28 wherein the electrocatalyst is characterized by the empirical formula $Pt_xRu_yPd_zOs_{1-x-y-z}$ where x is from about 0.20 to about 0.60, y is from about 0.10 to about 0.40, and z is from about 0.05 to about 0.35.

30. The fuel cell of claim 29 where the difference between 1 and the sum of y and z is from about 0.45 to about 0.65.

31. The fuel cell of claim 29 where the sum of y and z is from about 0.30 to about 0.60.

32. The fuel cell of claim 28 wherein the electrocatalyst is on the surface of the proton exchange membrane and in contact with the anode.

33. The fuel cell of claim 28 wherein the electrocatalyst is on the surface of the anode and in contact with the proton exchange membrane.

34. A method for the electrochemical conversion of a hydrocarbon-based fuel and oxygen to water, carbon dioxide and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane electrolyte therebetween, an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrocarbon-based fuel with a metal alloy catalyst to catalytically oxidize the fuel, the catalyst comprising platinum, ruthenium, palladium and osmium.

5 35. The method of claim 34 wherein the sum of the concentration of platinum and osmium, in atomic percent, is from about 40% to about 70%.

36. The method of claim 34 wherein the sum of the concentration of ruthenium and palladium, in atomic percent, is from about 35% to about 55%.

5 37. The method of claim 34 wherein the concentration, in atomic percent, of platinum is from about 40% to about 50%, the concentration of ruthenium is from about 15% to about 30%, the concentration of palladium is from about 20% to about 30%, and the concentration of osmium is from about 5% to about 14%.

1 / 3

FIG. 1

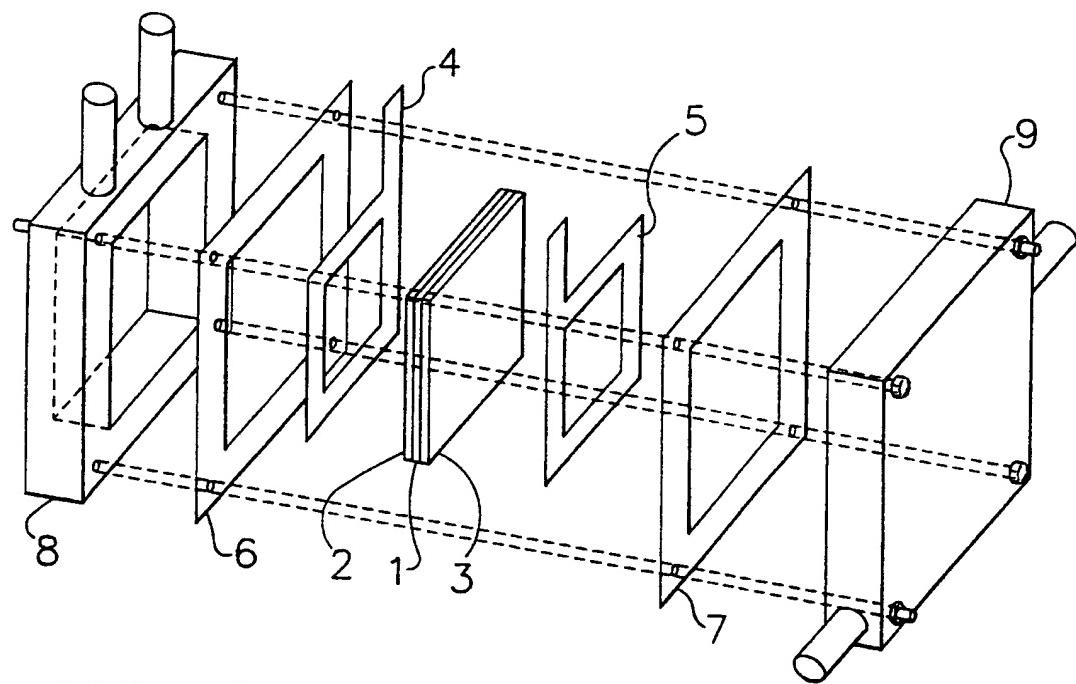
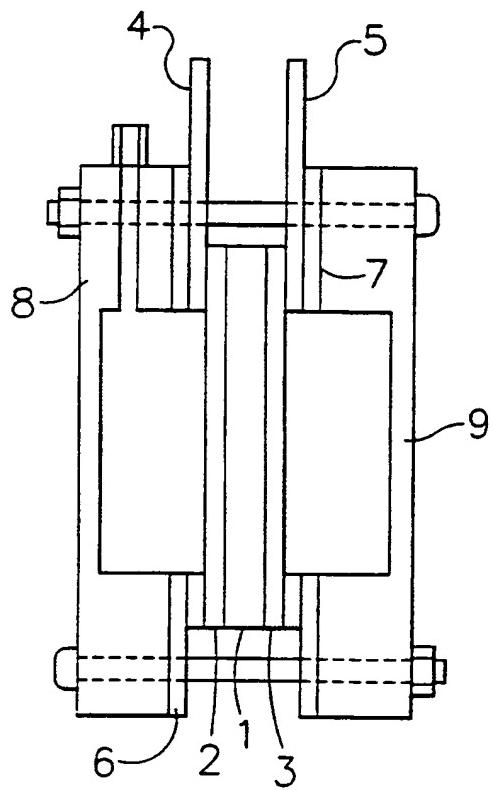


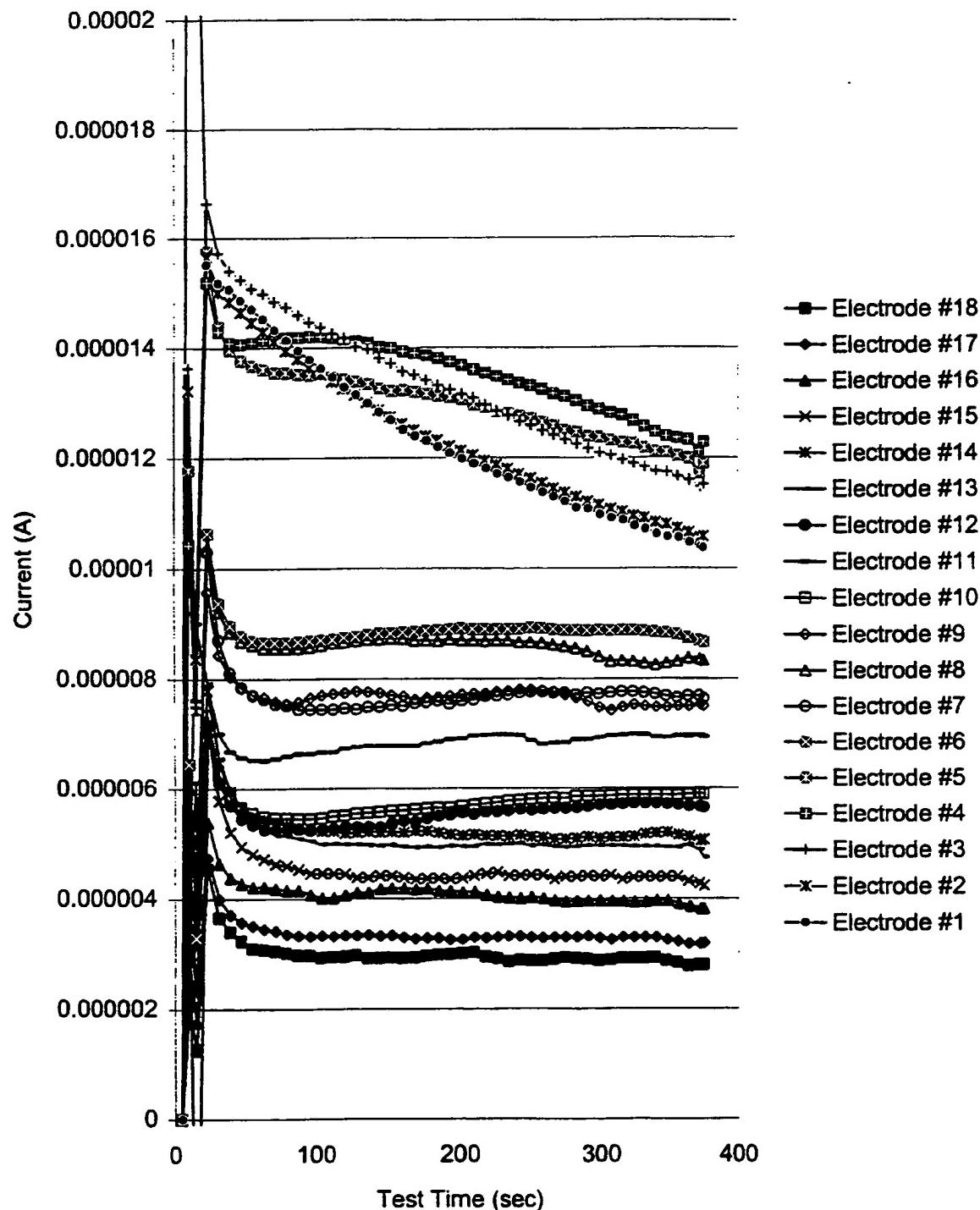
FIG. 2



2 / 3

FIG. 3

Methanol Oxidation Currents of Electroplated Alloy Compositions
-0.3 V vs. NHE

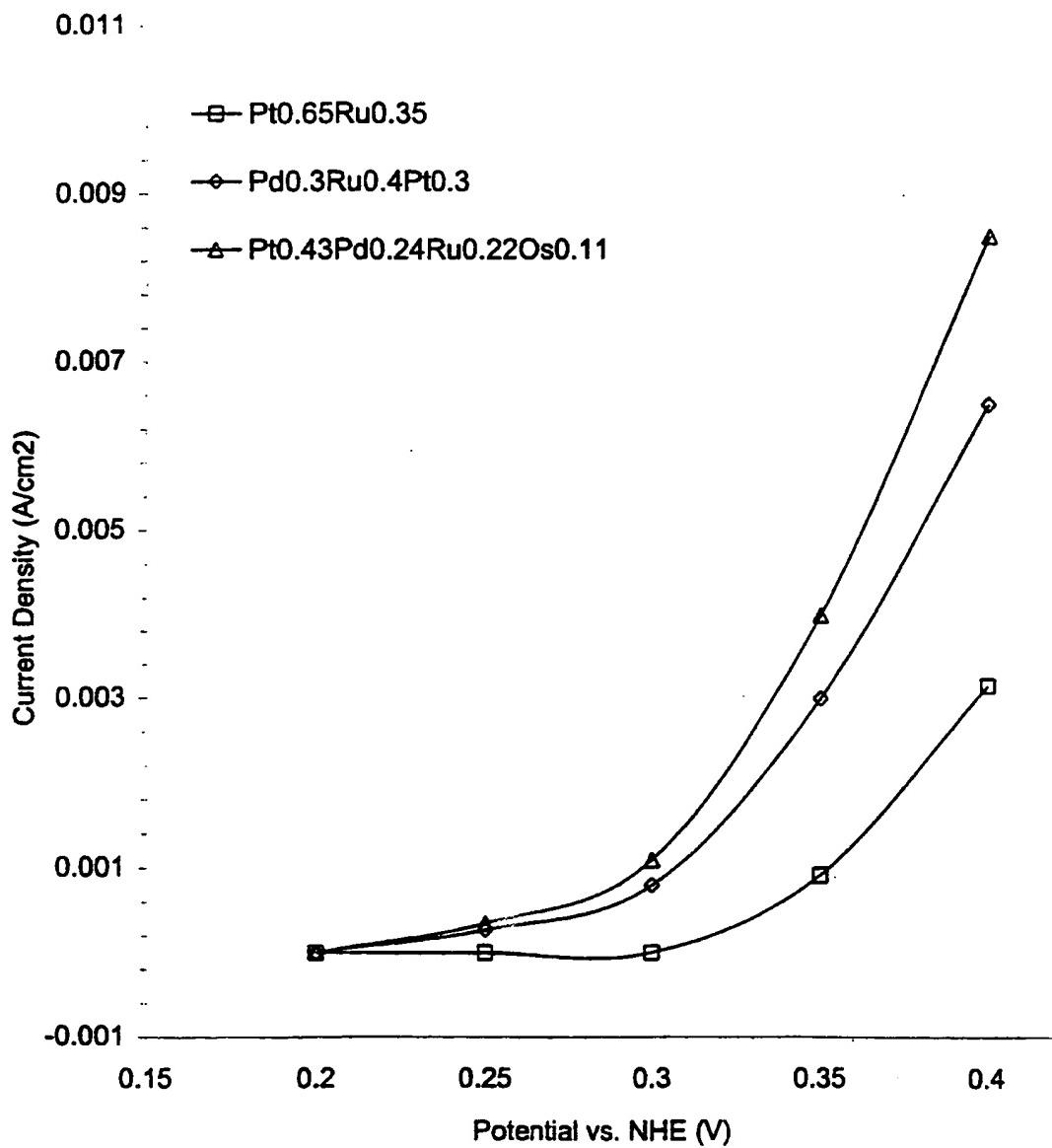


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3 / 3

FIG. 4

Current Density as a Function of Voltage
Measured in Aqueous Methanol (0.1M) and H₂SO₄ (0.5M)



INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/US 00/11327

A. CLASSIFICATION OF SUBJECT MATTER					
IPC 7	H01M4/92	H01M8/10	B01J23/42	B01J23/46	B01J23/44
C22C5/04					

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M B01J C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 690 119 A (EXXON RESEARCH ENGINEERING CO) 3 January 1996 (1996-01-03) claims 1-11	1-37



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
6 December 2000	12/12/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Battistig, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

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